Calculations from other work make it probable that a similar ratio holds at very low pressures.

5. It was shown that a gas admitted to another already adsorbed by charcoal replaces it rapidly at first, then with increasing slowness, and that replacement never goes so far as to give an amount of the second gas adsorbed equal to that which would be adsorbed from a mixture of the same composition mixed before being admitted to the charcoal.

6. A considerable lag in the adsorption isotherm obtained from carbon dioxide leaving charcoal compared with that obtained when the gas was entering it was detected; the lag amounted at its maximum to 5%.

7. The problem of the analysis of mixtures of carbon dioxide and nitrous oxide was satisfactorily worked out.

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THE SOLUBILITY OF POTASSIUM PERCHLORATE IN SALT SOLUTIONS AND THE CORRESPONDING ACTIVITY RELATIONS

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Introduction

Activity values may be derived, as is well known, from the solubilities of salts in solutions of other salts through the following considerations. In any solution saturated at a definite temperature with a uni-univalent salt such as AB the product of the activities $a_A \times a_B$ of the ion constituents A and B has a constant value whatever other salts may be in the solution. Expressing the concentration of the ion constituents by c with appropriate subscripts and putting the activity coefficient $\alpha = a/c$, we may write for any such solution

$$c_A\ \alpha_A\ c_B\ \alpha_B = \text{a constant, or } \frac{\alpha_A\ \alpha_B}{\alpha_{A0}\ \alpha_{B0}} = \frac{c_{A0}\ c_{B0}}{c_A\ c_B}$$

where the subscripts zero refer to the solution in pure water. Hence from solubility data the change can be determined of the activity-coefficient product with the nature and concentration of an added salt, or with the total concentration of the solution.

The purpose of the work described in this paper was to determine to what extent the activity-coefficient product for potassium perchlorate is dependent on the nature of the ions added to the solution. The ions for which the effect has been determined are: K^+, Na^+, Ba^{++}, Cl^-, NO_3^-, ClO_4^-, SO_4^{--}, the added salts producing these ions being KCl, KNO_3, K_2SO_4, NaCl, $NaNO_3$, $NaClO_4$, Na_2SO_4, $BaCl_2$, and $Ba(NO_3)_2$. The total concentrations of the saturated solutions were carried as high as 0.7–0.8 *N*.

This work was carried out at the suggestion and with the advice of Professor A. A. Noyes, to whom I wish to express my appreciation. It was assisted financially by a grant made to him from the Carnegie Institution of Washington.

Method of Determining the Solubility

Solubilities were determined at 25°, following the method previously used by Noyes and Boggs.[1] Potassium perchlorate was recrystallized until no test for chloride ion or chlorate ion was obtained, one recrystallization being usually sufficient. Other salts were of good commercial "analyzed" quality once recrystallized, with the result that in salts other than chlorides no chloride could be detected. The salt contents of the solutions were determined by evaporating a weighed portion on a steam-bath and drying the residue to constant weight at 200°. After the solutions were saturated with potassium perchlorate, they were filtered within the thermostat, and the total salt in them determined by evaporating and weighing. Knowing the amount of salt associated with a given amount of water in each salt solution, the amount of perchlorate in the saturated solution was determined by the difference.

Saturation was approached from both the under- and over-saturated sides in the case of about half the solutions; but as no systematic difference could in any case be detected, the other determinations were made without regarding the method employed.

The Solubility Data

The results of the solubility determinations are given in Table I. The salt contents are all expressed in equivalents of salt per 1000 g. of water. The values at the foot of each section of the table are means of the (usually) four separately determined values above them.

TABLE I

THE SOLUBILITY OF POTASSIUM PERCHLORATE IN SOLUTIONS OF OTHER SALTS AT 25°

$NaCl$	$KClO_4$	KCl	$KClO_4$	$NaClO_4$	$KClO_4$	$NaNO_3$	$KClO_4$	Na_2SO_4	$KClO_4$
.1006	.1567	.0985	.1138	.1027	.1117	.1008	.1610	.1047	.1633
.1007	.1566	.0983	.1135	.1026	.1123	.1008	.1610	.1047	.1633
.1007	.1568	.0980	.1135	.1025	.1123	.1007	.1611	.1047	.1634
.1008	.1568	.0984	.1136	...	.1122	.1008	.1612	.1048	.1626
.1007	.1567	.0983	.1136	.1026	.1122	.1008	.1611	.1047	.1633
.2995	.1659	.2993	.0758	.3091	.0751	.3141	.1789	.3210	.1801
.2991	.1659	.2995	.0757	.3088	.0752	.3138	.1791	.3211	.1802
.2992	.1657	.2995	.0751	.3090	...	.3140	.1780	.3209	.1800
.2991	...	.2995	...	...	...	.3138	.1790	.3210	.1799
.2994	.1558	.2994	.0757	.3090	.0752	.3139	.1790	.3210	.1800

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[1] Noyes and Boggs, THIS JOURNAL, **33**, 1650 (1911).

.5906	.1732	.6089	.0534	.6273	.0532	.6218	.1995	.6610	.1954
.5903	.1732	.6087	.0536	.6273	.0535	.6221	.1993	.6610	.1959
.5901	.1732	.6089	.0529	...	...	...	.1994	.6610	...
.5901	.1730	.6090	.0535	...	...	...	.1992	.6610	...
.5903	.1732	.6089	.0535	.6273	.0533	.6220	.1994	.6610	.1957

KNO_3	$KClO_4$	K_2SO_4	$KClO_4$	$BaCl_2$	$KClO_4$	$Ba(NO_3)_2$	$KClO_4$
.0971	.1174	...	...	.0991	.1569	.0988	.1612
.0971	.1175	...	...	.0991	.1569	.0991	.1592
.0971	.1173	...	...	...	...	...	.1612
...	.1175	...	...	...	...	...	...
.0971	.1174	.0998[a]	.1194[a]	.0991	.1569	.0990	.1605
.2955	.0844	.3024	.0857	.2975	.1637	.3019	.1756
.2953	.0847	.3026	.0857	.2971	.1638	.3016	.1726
.2953	.0848	.3025	.0855	.2974	...	.3021	.1760
...	.0844	...	...	...	...	.3018	...
.2954	.0846	.3025	.0857	.2974	.1638	.3019	.1747
.6686	.0641	.6011	.0641	.5996	.1692	.6074	.1896
.6687	.0654	.6004	.0644	.5995	.1694	.6077	.1907
.6686	.0639	.6005	.0649	...	...	.6076	...
...	.0636	.6012	...	...	...	.6073	...
.6686	.0642	.6008	.0644	.5995	.1693	.6075	.1902

[a] Derived from the results of Noyes and Boggs, Ref. 1.

The Values of the Activity Coefficient

Table II contains the mean values of the solubility, transferred from Table I, the salt content being here expressed in milli-equivalents per 1000 g.

TABLE II

THE VALUES OF THE ACTIVITY-COEFFICIENT PRODUCT

Added salt				Added salt			
Nature	Content	Solubility	Act.-coef. product	Nature	Content	Solubility	Act.-coef. product
None	0	149.1	1.000	None	0	149.1	1.000
KCl	98.3	113.6	0.923	K_2SO_4	99.8	119.4	0.849
	299.4	75.7	.783		302.5	85.7	.668
	608.9	53.5	.627		600.8	64.4	.519
KNO_3	97.1	117.4	.883	Na_2SO_4	104.7	163.3	.834
	295.4	84.6	.691		321.0	180.0	.686
	668.6	64.2	.490		661.0	195.7	.580
$NaClO_4$	102.6	112.2	.922	$BaCl_2$	99.1	156.9	.903
	309.0	75.2	.769		297.4	163.8	.829
	627.3	53.3	.613		599.5	169.3	.776
NaCl	100.7	156.7	.905	$Ba(NO_3)_2$	99.0	160.5	.875
	299.4	155.8	.809		301.9	174.7	.728
	590.3	173.2	.741		607.5	190.2	614
$NaNO_3$	100.8	161.1	.857				
	313.9	179.0	.694				
	622.0	199.4	.559				

of water. The last column of each half of the table contains the activity-coefficient product, $\alpha_A\alpha_B/\alpha_{A_0}\alpha_{B_0}$, calculated from the inverse solubility-product ratio, $c_{A_0}c_{B_0}/c_Ac_B$, in accordance with the principles described in the Introduction of this article.

Discussion of the Results

The logarithm of the activity-coefficient product is plotted against the logarithm of the total salt content in Fig. 1. The striking fact shown by the graphs is that each added ion has a specific effect independent of the other ion with which it is associated. Thus potassium ion has a much greater effect than sodium or barium ion in reducing the activity-coefficient product of potassium perchlorate, and the sodium ion has an only slightly greater effect than barium ion, these statements being true whether these ions are present with chloride, nitrate, or sulfate ion (in the cases of potassium and sodium ion). Similarly, chloride ion always exerts a much smaller effect than nitrate or sulfate ion, while the last two ions have nearly the same influence.

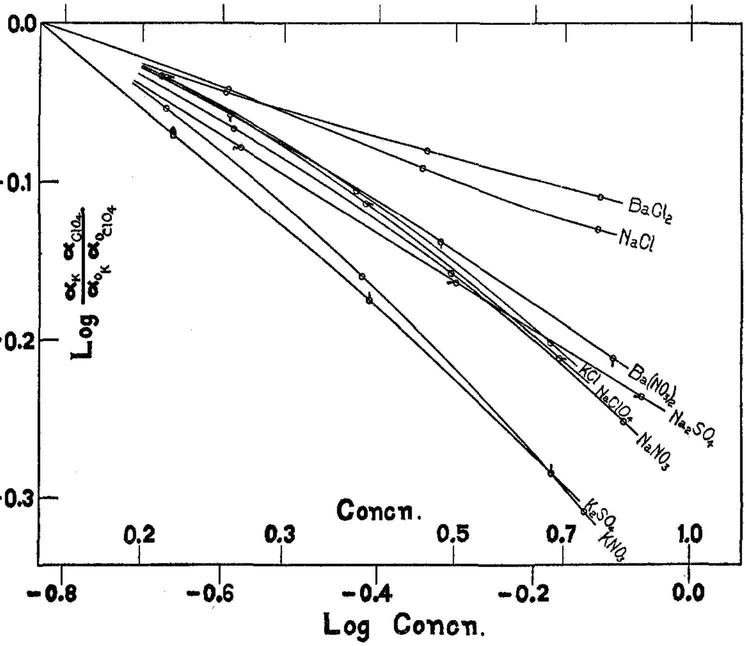

Fig. 1

These effects are clearly brought out also by the values shown in Table III of the activity-coefficient product interpolated for a total concentration of 0.5 *N*. The differences in the product caused by replacing one ion by another are seen to have a definite value no matter what ion of opposite sign is present with the two ions to be compared; for example, the difference in the activity-coefficient product caused by replacing potassium by sodium is about 0.09 whether the potassium and sodium are associated with chloride, nitrate or sulfate.

TABLE III

VALUES OF THE ACTIVITY-COEFFICIENT PRODUCT AT A TOTAL CONCENTRATION OF 0.5 NORMAL

Salt added	Activity product	Difference	Salt added	Activity product	Difference	Salt added	Activity product	Difference
KCl	0.705		KNO_3	0.600		K_2SO_4	0.597	
		0.093			0.090			0.089
NaCl	.798		$NaNO_3$	.690		Na_2SO_4	.686	
		.023			.027			
$BaCl_2$	.821		$Ba(NO_3)_2$	.717				
KCl	.705		NaCl	.798		$BaCl_2$	.821	
		.105			.108			.104
KNO_3	.600		$NaNO_3$	.690		$Ba(NO_3)_2$	.717	
		.003			.004			
K_2SO_4	.597		Na_2SO_4	.686				

These results show that the effects of the different ions are specific and additive at the fairly large concentrations (0.25–0.75 *N*) here prevailing. These specific effects are so marked as to hide any influence of the valence of the added ion; thus at the same normality barium ion has not far from the same effect as sodium ion, but a much less effect than potassium ion, and sulfate ion has nearly the same effect as nitrate ion, but a much greater effect than chloride ion.

Summary

The solubilities of potassium perchlorate have been determined in 0.1, 0.3, and 0.6 *N* solutions of the salts KCl, KNO_3, K_2SO_4, NaCl, $NaNO_3$, $NaClO_4$, Na_2SO_4, $BaCl_2$ and $Ba(NO_3)_2$. The individual effects of the separate ions on the activity-coefficient product of the potassium and chlorate ions have been compared, and at the concentrations involved (0.25–0.75 *N*) have been found to be markedly specific and additive.

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